THE NATURE OF VITRINITE SECONDARY FLUORESCENCE

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INTRODUCTION

In recent years, the phenomenon of vitrinite fluorescence has been noted and related to thermoplastic behavior (1-5). Huminite/vitrinite fluorescence can be divided into primary and secondary stages of fluorescence. Primary vitrinite fluorescence is inherited from biopolymers; it decreases markedly in intensity from the peat stage to the subbituminous C/B rank and, within the same range, the wavelength of its maximum spectral intensity shifts from 520 to 660 nm. Following the loss of most of the primary fluorescence, a secondary vitrinite fluorescence begins to develop, and this in turn becomes extinct at low volatile bituminous rank (ca. 1.8% Rm) (4). It is the secondary vitrinite fluorescence, within the bituminous rank range, which is well correlated with thermoplastic properties.

Although the fluorescence of all coal macerals has been the subject of intensive study during recent years, the chemical basis of the phenomenon is little understood. Teichmüller(3-4) has attributed the secondary fluorescence of vitrinite to the presence of absorbed "bitumen" which has been generated during coalification from liptinite and lipoid substances incorporated in the vitrinite. Ottenjann et al.(2) noted the parallelism between vitrinite fluorescence and solvent extraction yields, and also suggested that the fluorescence is due to the presence of "bitumen". Of course, this idea was speculative and required further chemical confirmation.

Recent studies(6-10) of the structure of vitrinite suggest that this maceral can be regarded as occurring in two distinct phases. One is considered to be a relatively more condensed three-dimensional aromatic network system. The other, called "mobile phase", is thought of an assembly of relatively small molecules located, even partly trapped, within the network.

In the present work, coal extracts have been obtained by a series of Soxhlet extractions of coals with solvents of decreasing strength. HPLC has been used to further separate the "oil" (hexane-soluble) into aliphatic, aromatic and polar fractions. Each component and fraction was examined by reflected blue-light microscopy to determine which are actively fluorescent.

In order to study the development of the mobile phase as a result of coalification, and the associated changes in secondary fluorescence and thermoplastic behavior, a suite of 14 coals was tested. The spectral fluorescence characteristics of the vitrinite, yield of chloroform-soluble material, and the Gieseler fluidity of all these coals have been measured.

EXPERIMENTAL

Coal Samples

The fourteen coals used in these experiments were obtained from the Penn State Coal Sample Bank; they had been stored in a nitrogen atmosphere at minus 20 mesh size. Table I lists some compositional data for these coals.

Table 1

Sample number (PSOC)	Romax (%)	Petrographic composition (dmmf)			Sample number (PSOC)	Romax (%)	Petrographic composition (dmmf)		
		V	I	E			V	I	E
773	0.54	91.0	5.7	3.3	1198	1.45	89.4	10.4	0.2
780	0.70	89.8	9.5	0.7	1136	1.53	89.7	10.3	0.0
779	0.73	90.4	8.1	1.5	1330	1.75	92.1	7.9	0.0
1296	0.87	91.6	3.8	4.6	1281	0.63	84.1	7.2	8.7
1299	0.93	91.9	6.2	1.9	1142	0.88	87.0	8.7	4.3
815	0.97	91.5	3.9	4.6	1336	0.92	85.1	10.1	4.8
1196	1.30	89.6	10.4	0.0	1340	1.01	80.4	9.1	10.5

Solvent Extraction and Fractionation

Coal samples were ground to minus 60 mesh in a glove box in which a flow of nitrogen was maintained. Moisture was removed at 60° C overnight in a vacuum oven. Approximately 5 g of dried coal samples were extracted for 48 h in a Soxhlet apparatus fed with a stream of nitrogen. The resulting extracts and residues were vacuum dried for 12 h to remove any solvent. Fig. 1 is a flow chart of the progressive solvent extraction and fractionation scheme employed. Pyridine and chloroform extractions were performed at the solvent boiling points; the chloroform soluble fraction was then separated into the oil and asphaltene fractions with hexane at room temperature.

The HPLC fractionation of the "oil" was performed with a Waters Associates' instrument equipped with a semi-preparative Whatman column (Partisil Magnum 9/50 PAC). The oil was dissolved in hexane and injected into the sample loop. Separation of three fractions is based on the absorbance response detected (Fig. 2). The aliphatic and aromatic fractions were the first two fractions to be eluted, in that order. Finally, by using the back flush valve and eluting a small amount of methylene chloride, the polar fraction was collected from the column.

Fluorescence Microscopy

The fluorescence examinations and measurements were performed with a Leitz MPV-II microscope system equipped with the following accessories:

i) HBO 100-watt ultra-high pressure mercury lamp;
ii) Ploempak 2.1 vertical illuminator with a BD 390-490/RKP510 LP515 filter for qualitative examination and a BP340-380/RKP400 LP430 filter for quantitative measurement;
iii) Double grating monochromator;
iv) Water-cooled, broad spectral response photomultiplier; and
v) Calibration tungsten lamp, 12v, 100 watt, color temperature 3200K.

Data were processed with a PDP 11/02 computer. All measured spectra were corrected prior to analysis for both system variation and background interference. System variation was determined by measuring the deviation from the known spectrum of the calibration lamp. This correction permits compensation for any optical

distortion within the system. Background measurements taken from a non-fluorescing object, in this case fusinite, are employed to reduce the influence of the immersion oils' self-fluorescence and fluorescence interference from the epoxy resin binder. Corrected spectra were all adjusted to values of relative intensity. Identical electrical and optical configurations were employed for each sample series to provide comparable results. For final comparisons of spectral fluorescence, the spectra were normalized to 100% maximum fluorescence intensity.

To prepare the coal extracts and fractions for microscopic study, they were redissolved at low concentration in their corresponding solvents and a drop placed on a glass slide. The solvents were removed by drying in a flow of nitrogen. Glass cover slips were placed over the dried specimens for reflected blue-light study under oil immersion. Raw coals and the pyridine-insoluble fractions were molded into pellets with epoxy resin prior to polishing according to the ASTM procedure(11).

Gieseler Fluidity

The fluid behavior of the coal samples was tested with an automated Gieseler plastometer(12). For each run, 5 g of minus 40 mesh coal was packed into the cylinder. The cylinder assembly was heated in a solder bath and heated from 330°C at 3°C/min. Because of the very high fluidity displayed by some Lower Kittanning samples a torque of 20 g-in. was used rather than the standard 40 g-in. (9.96 mN/m).

THE ORGANIC CHEMISTRY OF FLUORESCENCE

Aliphatic Compounds

Very few aliphatic and saturated cyclic organic compounds fluoresce. Saturated hydrocarbons like ethane, hexane and cyclohexane and simple unsaturated hydrocarbons like ethylene display no visible or ultraviolet fluorescence(13). All electrons in aliphatic compounds are either very tightly bound or are involved in sigma bonding. The absorption of ultraviolet energy by a saturated molecule usually results in bond dissociation. Important exceptions are the aliphatic aldehydes and ketones; in these, the non-bonding electrons on the carbonyl oxygen can be excited to antibonding C=O π orbitals without severe disruption of molecular bonding(14). Some polyenes also give a visible fluorescence(13,15).

Aromatic Compounds

The majority of fluorescing organic compounds are those possessing large conjugated systems, in which there are electrons less strongly bound within the molecule than sigma electrons, and heteroatoms (N, O, S, etc.), in which n electrons, can be promoted to antibonding orbitals by absorption of excitation energy. Hence, the aromatics and polars should be our main concerns.

Most aromatic compounds are fluorescent. The condensed aromatics, of which vitrinite is largely composed, can be subdivided into linearly and nonlinearly condensed aromatics. Linearly condensed aromatics are those in which benzene rings are fused in a straight chain; their fluorescence displays an increasing wavelength with increase in the number of rings and of conjugated double bonds(15). This is brought about by a decrease in the energy difference between the lowest excited state and the ground state. The fluorescence generated decreases markedly for aromatic hydrocarbons containing more than three phenyl rings in a straight chain. Nonlinearly condensed aromatics generally do not follow this trend. Their fluorescence is very dependent on molecular configuration. But it is generally true that the fluorescence is at longer wavelengths in compounds containing larger ring systems, although there are some exceptions(16).

Polar Compounds

Polar compounds which are derived from aromatic hydrocarbons by substitution are fluorescent mostly because of the existence of n electrons in heteroatoms or polar functional groups (-SH, -OH, $-NH_2$). The fluorescence of aromatic hydrocarbons is usually altered by ring substitution. The substitution of these polar functional groups or heteroatoms onto the aromatic molecule usually causes a shift into longer wavelengths(13-15). Consequently, these compounds generally fluoresce in a longer wavelength regime than the corresponding aromatic molecules.

FLUORESCENCE OF THE VITRINITE EXTRACTS AND FRACTIONS

HPLC Fractions

Aliphatics: As observed under the microscope, this fraction is mostly non-fluorescent. Aliphatic compounds usually have a fluorescence quantum yield (defined according to Becker(16) as the quanta emitted per exciting quantum absorbed) of zero, because of the types of electron bonding described above. However, a small portion of this fraction displays a fluorescence which has a spectral peak at 450 nm or below and decreases progressively at longer wavelengths (Fig. 3). The spectral distribution is very similar to that of the aromatics, although the intensities are quite different. Several possibilities may account for the fluorescence of this small portion of the aliphatic fraction:

i) aliphatic aldehydes or ketones;
ii) aliphatic polyenes;
iii) aromatic impurities resulting from imperfect fractionation.

Aromatics: This fraction is very highly and actively fluorescent. The fluorescence spectrum has a peak at 450 nm or just below and decreases in intensity with increasing wavelength (Fig. 3).

Compounds which have been used as standards for HPLC fractionation of aromatics include: fluorene; naphthalene; phenanthrene; 3,4-benzo-(a)-pyrene; 9, 10-benzo-phenanthrene; 9, 10-dihydroanthracene; 2, 3-dimethylnaphthalene and 1-phenylheptane(17). The spectral fluorescence of some of these compounds (fluorene, anthracene and naphthalene) as well as that of chrysene have been reported by Hagemann and Hollerbach(18). These spectra also peak at short wavelengths, from 430 to 450 nm, and have a similar distribution to those of coal-derived aromatics. It is suggested that the aromatic fractions obtained in the present study are composed of similar molecules; the actual spectra represent the overlapping fluorescence responses of such compounds.

Polars: Like the aromatics, this fraction is also very highly and actively fluorescing. Although the spectrum in this particular case (Fig. 3) is doubly peaked, other coals have yielded dissimilar spectra. The first peak here occurs at 490 nm, and the second, which is the maximum, at 660 nm. A close similarity exists between the spectral distribution of this fraction and that of the oil from which the polars are derived (Fig. 4). The peaks for the polar fraction occur at 30 nm higher, and the maximum is at the longer wavelength.

Oil (hexane soluble)

The fluorescence spectrum of this component also is doubly peaked; the maximum occurs at 460 nm, and a second peak at 627 nm (Fig. 4). The shift of the peak positions to a longer wavelength in the case of the polar fraction may be due to the substantial absence of aromatic substances which have fluorescence peaks at very short wavelengths. As mentioned earlier, substitution of polar functional groups onto the aromatic structure can result in a red shift of the spectrum.

Asphaltene (hexane insoluble)

The spectrum for this fraction peaks at 690 nm (Fig. 4). The aromatics in this fraction are relatively more condensed than those in the oil fraction; hence, their fluorescence spectra peak at longer wavelengths.

γ-Fraction (chloroform soluble)

This component has a heterogeneous fluorescence even at very small concentrations. At least three different fluorescence entities can be recognized (Fig. 5). The wavelengths of the maximum fluroescence intensities of these three entities are 562, 627 and 698 nm. Entities 1 and 2 appear to correspond to the "oil", and entity 3, whose spectrum peaks at a longer wavelength, appears to be composed of asphaltene-like material according to their fluorescence characteristics.

β-Fraction (chloroform insoluble fraction of pyridine solubles)

The fluorescence of this fraction has a very similar spectral distribution to those of the untreated vitrinite and the pyridine extracts and residues, but has a lower intensity (Fig. 6). The lower intensity probably can be attributed to the removal of chloroform-soluble materials, which are actively fluorescent. The β-fraction is primarily composed of relatively more condensed aromatics, which may have been derived from the network disintegration.

α-Fraction (pyridine insoluble) and Pyridine-Soluble Fraction

These two fractions and the Vitrinite in the unextracted coal have very similar spectral distributions (Fig. 6). This is consistent with the results that pyridine extracts are chemically similar or identical to the pyridine-insoluble residue; the nature of these two fractions closely resemble that of the parent coal(19).

Vitrinite

The spectrum of this maceral is very similar to that of the pyridine extract and residue as discussed above (Fig. 6). There are, however, differences in fluorescence intensity between the untreated vitrinite and the pyridine extract and residue which are not fully understood. Further studies are being conducted.

The Aromatic Network

The fluorescence of this phase cannot be directly investigated because of our inability to completely separate the mobile phase from the aromatic network system without modifying the structure of the latter. The following indirect lines of evidence suggest that the network system is too condensed to show visible fluorescence in coals beyond the subbituminous B stage:

i) Huminite/vitrinite primary fluorescence is lost when the coal rank reaches subbituminous C/B stage. This indicates that any inherited chemical structure, for example that derived from lignin, would be too condensed to have a visible fluorescence,
ii) More condensed aromatics generally have a relatively low fluorescence intensity and a longer wavelength of maximum fluorescence intensity,
iii) Highly aromatized systems such as fusinite, anthracitic macerals and coals carbonized at temperatures greater than 500-600°C do not visibly fluoresce,
iv) The fluorescence of coked anthracene shifts into the longer wavelength region and decreases in intensity with increased coking temperature.

FLUORESCENCE CHARACTERISTICS AND FLUID BEHAVIOR OF A COAL RANK SUITE

Vitrinite primary fluorescence is lost as the rank increases beyond subbituminous C/B stage. At this stage, the secondary fluorescence begins to develop, the intensity of which increases up to the high volatile A bituminous stage (ca. 0.9% Ro max). Beyond this rank, fluorescence intensity decreases markedly(4). This trend for vitrinite fluorescence corresponds to changes in the yield of chloroform extracts and the maximum Gieseler fluidity displayed by the coals (Fig. 7).

Within the sub C/B-hvAb range just discussed the proportion of mobile phase has been built up. Possible contributions to the development of this mobile phase have resulted from:

i) oligomerization associated with the network polymerization,
ii) migration of petroleum-like substances derived from liptinites and lipoid substances(3-4).

At high volatile A bituminous rank, where secondary fluorescence, chloroform yield and fluidity all reach a maximum level, the wavelength of maximum fluorescence has been shifted into the infrared region(4). At higher ranks, the maximum intensity in the visible region decreases (Fig. 7). This, and the associated decreases in chloroform yields and fluid behavior is related to the gradual cracking of the mobile phase into gaseous products that accompanies aromatic condensation. These conclusions are consistent with the observation that the fluorescence of chloroform extracts undergoes a red shift with increasing rank(18).

The visible fluorescence of vitrinite is finally lost at low volatile bituminous rank (above 1.8% Ro max)(4). This corresponds to a loss of fluid behavior and a very low chloroform extraction yield.

SUMMARY AND CONCLUSIONS

Vitrinite can be considered to be composed of two phases: a mobile phase and a network phase (Fig. 8). The mobile phase contains actively and highly fluorescent aromatics, polar groups and a small proportion of aliphatic groups. These fractions absorb excitation energy and emit a part of this energy as fluorescence. The fluorescence spectra of these separate fractions are very different from those where they are combined in a complex system like vitrinite. This is because of both intramolecular and intermolecular interaction between the fluorescing molecules and the molecules in the network environment. This interaction can cause a certain degree of fluorescence quenching. As a result the fluorescence of vitrinite has a much lower intensity and a longer wavelength than those of the mobile phase fractions which it contains. So, the aromatic network system, which acts as the host for the fluorescing molecules in the mobile phase, though not actively fluorescent in the visible region, influences the overall vitrinite fluorescence character.

The build-up of the mobile phase in the bituminous rank range results in the maximum development of vitrinite secondary fluorescence, and is also manifested in optimum chloroform extraction yields and fluid behavior.

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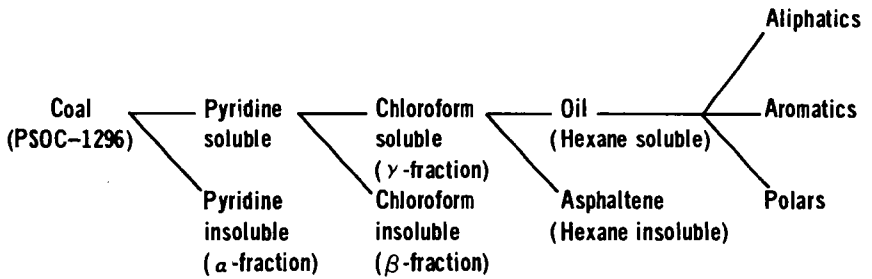

Figure 1. Solvent Extraction and Fractionation Scheme

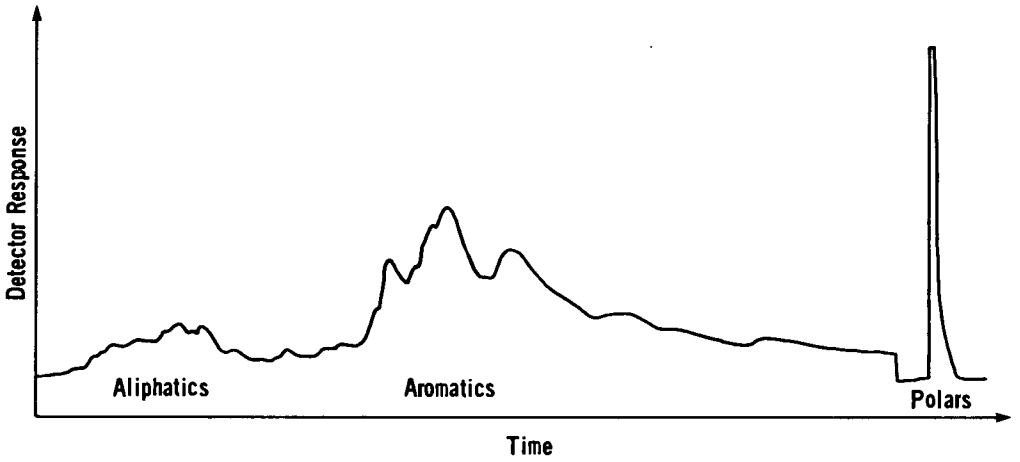

Figure 2. Absorbance Response of HPLC Fractions

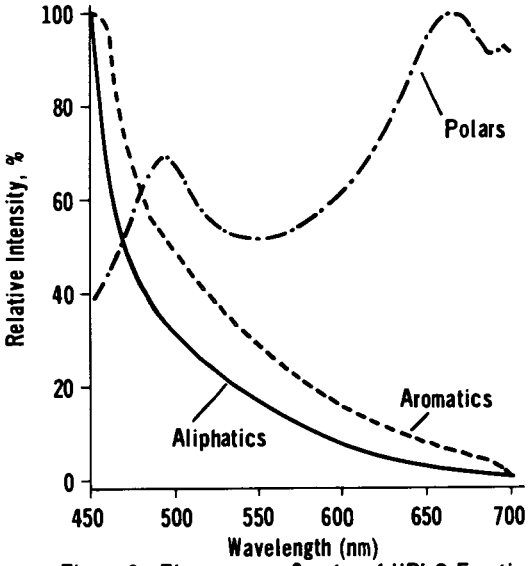

Figure 3. Fluorescence Spectra of HPLC Fractions

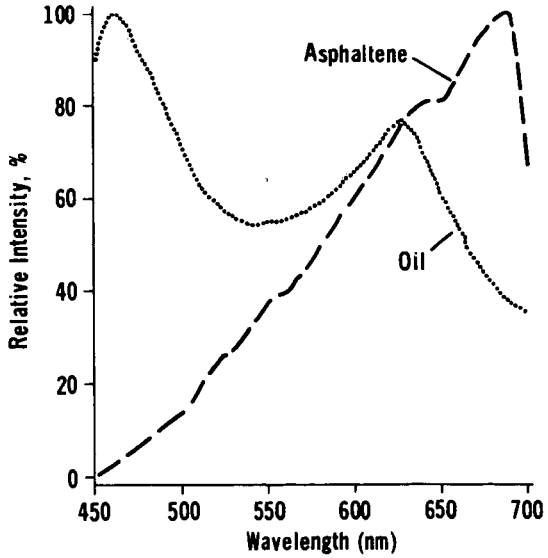

Figure 4. Fluorescence Spectra of Oil and Asphaltene

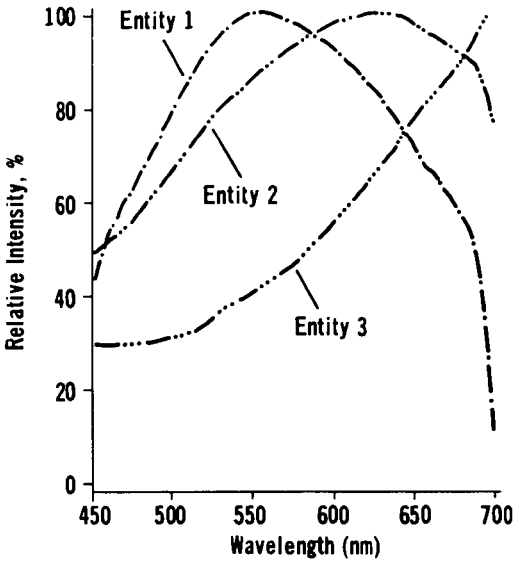

Figure 5. Fluorescence Spectra of Three Entities in γ-fraction

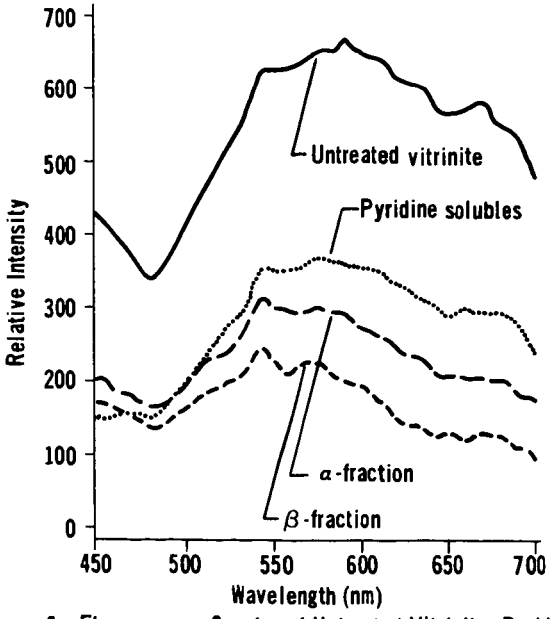

Figure 6. Fluorescence Spectra of Untreated Vitrinite, Pyridine Solubles, α-fraction and β-fraction

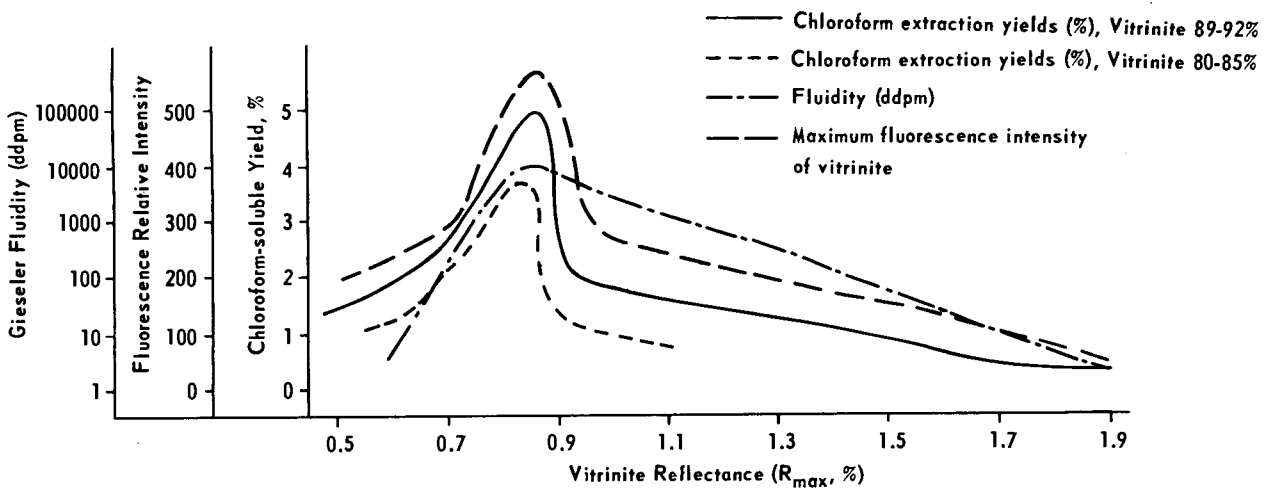

Figure 7. Relations among Fluorescence Intensity, Chloroform Extraction Yields and Fluidity for Coals of Different Rank

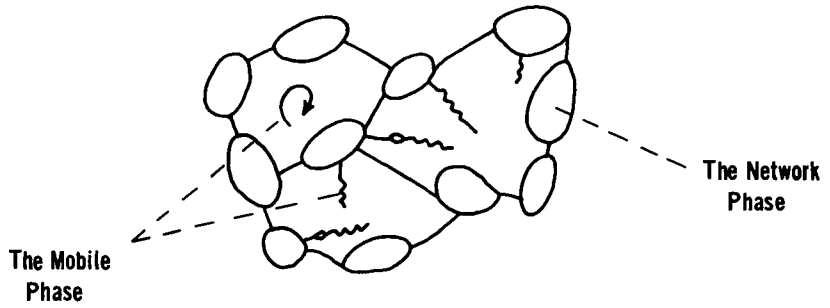

Figure 8. Two-phase Model of Vitrinite Structure
(Modified after Given and Derbyshire (6) and Neavel (20))